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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/FI92/00081 (22) International Filing Date: 23 March 1992 (23.03.92) (30) Priority data: 912262 9 May 1991 (09.05.91) FI (71) Applicant (for all designated States except US): NESTE OY [FI/FI]; P.O. Box 310, SF-06101 Porvoo (FI).	(74) Agent: BERGGREN OY AB; P.O. Box 16, SF-00101 Helsinki (FI).  (81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), NO, SE (European patent), US.	
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(54) Title: A PROCATALYST FOR POLYMERIZATION OF OLEFINS CONTAINING A TRANS-ESTERIFICATION PRODUCT OF A LOWER ALCOHOL AND A PHTHALIC ACID ESTER  (57) Abstract  In the invention a procatalyst composition intended for the polymerization of olefins has been provided, which has been prepared by bringing together magnesium chloride, a lower alcohol, a titanium compound and an ester of phthalic acid. The procatalyst composition is active and stereospecific and it simultaneously has a titanium and phthalic acid content as low as possible. These good properties have been achieved by carrying out a trans-esterification between the lower alcohol and the ester of the phthalic acid, whereby the alkoxy group of the phthalic acid comprises at least five carbon atoms.		

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A procatalyst for polymerization of olefins containing a trans-esterification product of a lower alcohol and a phthalic acid ester.

5 The invention relates to a procatalyst composition intended for the polymerization of olefins, which has been prepared by bringing together  $MgCl_2$ , a lower alcohol, a titanium product and an ester of phthalic acid. The invention also relates to the use of said procatalyst composition for the  
10 polymerization of propylene.

Olefins, especially  $\alpha$ -olefins, are often polymerized by the aid of a catalyst composition, in which the procatalyst is formed by a compound of a transition metal of the groups IV-  
15 VI of the periodic table and a compound of a metal of the groups I-III of the periodic table, activating it by reduction, i.e. the co-catalyst. The so-called Ziegler-Natta-procatalyst has been further developed by using as the support of the transition metal an inert carrier, to which  
20 the transition metal compound is layered with the intention to thus improve the activity of the procatalyst when it is catalyzing the polymerization reaction.

Yet, influenced by this procatalyst composition, the asymmetrical olefin monomers often polymerize to various kinds of stereoisomeric polymers to form mixtures of e.g. isotactic, atactic and syndiotactic polymers, from which the desirable stereoisomer must be separated by means of often  
30 troublesome washing and other stages. When mainly a polymer of a certain stereospecific form is wished to be produced, e.g. an isotactic polyolefin from an asymmetrical olefin monomer, the influence of the catalyst to the stereospecificity has been improved by adding a donor compound to the catalyst. Because of a certain steric structure the  
35 donor compound contributes to the settling of the monomer molecule in a certain position in the catalyst particle at the end of the growing polymer molecule, thus giving the molecule chain of the polymer a certain stereoisomeric

structure and making the polymer product obtained, dependent on the donor compound selected, more and less as desired. There are two possibilities to add a donor to the catalyst: already to the procatalyst mixture of the transition metal compound and the carrier is added a so-called internal donor, or the donor is added to the mixture of the monomer and the catalyst component in the polymerization reactor only when the cocatalyst is added, whereby the donor is called an external donor. A donor compound can, of course, also be used in both stages, whereby the donor can be a similar or a different compound at the various stages.

To asymmetrical i.e. stereospecifically polymerizing monomers count all but ethylene, all side groups of the two non-saturated carbon atoms of which are hydrogens, and the rare case, where all side groups are similar, e.g. tetramethyl ethylene. A certain stereospecific form is made desirable by the fact that the properties of the polymer obtained for a certain purpose are more favourable, e.g. the isotactic polyolefins crystallize more easily, their bulk density is greater, their mechanical properties are better; thus they are e.g. stronger, etc. The adhesiveness of the atactic form, i.e. the adhesion properties, are generally better than in the tactic forms and they are thus suitable e.g. for glue applications.

When polymerizing asymmetric olefin monomers, i.e. the groups attached to carbon atoms attached by non-saturated bonds being of different kind at least as far as one group is concerned, the catalyst can comprise a compound improving the stereospecificity of the catalyst, i.e. an electron donor, which, as a donor of an electron, easily can attach to the resting structure of the catalyst and due to its steric influence direct the monomer molecule, which is going to attach to the polymer chain, to a position where the polymer molecule produced is, in a way, stereospecific as to its structure. Among such donors count a numerous amount of various organic compounds, among others esters, carboxylic acids, alcohols, ketones, aldehydes, nitriles, amides,

amines, organic phosphorus and silicon compounds, etc. These compounds also have other influences on the properties of the catalyst, e.g. the activity of the catalyst varies depending on the donor used. If the donor is an ester of carboxylic acid, usual are the esters of aromatic carboxylic acids, e.g. benzoates, phthalates, toluates, anisates, etc. The most preferable of these donors are the dialkyl phthalates.

Combinations of various donors are also known in the field. Thus, from the JP publications 59172507, 59206409, 59206415, 59206416, 59206424, 60262804, 61103910 and 61108614 is known a procatalyst composition, which is prepared from  $MgCl_2$ , 2-ethylene hexyl alcohol, titanium tetrachloride, di-isobutyl phthalate and in some cases from phthalic acid anhydride.

The patent family comprising the publications DE 3,540,699, EP 226,003 and US 4,761,461, discloses a procatalyst composition, which has been obtained by bringing together  $MgCl_2$ , alcanol, such as ethanol, an ester of phthalic acid, such as di-isobutyl phthalate, and titanium tetrachloride in certain conditions. The ester of phthalic acid can be added either at the stage when  $MgCl_2$  and ROH are reacting with each other, or at the stage when the reaction product of  $MgCl_2$  and alcanol are brought to react with titanium tetrachloride.

The high titanium content of the above-mentioned procatalysts causes colour problems in the polymers and the high phthalic acid content brings forth non-desirable aromatic residues in the polymers.

The aim of the invention is the provision of an active and stereospecific procatalyst composition, which simultaneously has a titanium and phthalic acid content as low as possible. The aim has now been achieved by the new procatalyst composition intended for the polymerization of olefins, which is mainly characterized by what is stated in the characterizing clause of Claim 1. It has, thus, been realized that when preparing a procatalyst composition by

bringing together  $\text{MgCl}_2$ , a lower alcohol, a titanium compound and an ester of phthalic acid a transesterification is simultaneously carried out between the lower alcohol mentioned and the phthalic acid, and an ester of phthalic acid is used, the alkoxy group of which comprises at least 5 carbon atoms.

A  $\text{MgCl}_2$  carrier can be used as such or it can be combined with silica, e.g. by absorbing the silica with a solution or slurry containing  $\text{MgCl}_2$ . It is also important that the  $\text{MgCl}_2$  used is pure and non-aqueous. The lower alcohol used can be any  $\text{C}_1$ - $\text{C}_2$  alkanol. Preferable alcohols are methanol and ethanol, particularly ethanol.

As, because of the replica phenomenon the physical structure of the catalyst carrier repeats itself in the whole catalyst composition and this then in the polymer product obtained, it is very important to make the physical structure of the carrier i.e. the morphology beneficial i.e. alike the desired product. This can be achieved by proceeding in two different ways, which can, of course, also be combined: chemically i.e. by treating the carrier with certain chemicals, or physically, i.e. by grinding the carrier in a ball mill or in a jet blower mill.

Also a procedure can be used in which an adduct of the carrier, in this case expressly the  $\text{MgCl}_2$ , and a lower alcohol, such as ethanol, is first prepared, which adduct is injected by means of gas into cold solvent or cold gas, whereby the adduct crystallizes to a morphologically preferable form and this crystalline adduct is used as a catalyst carrier (cf. FI-862459).

The titanium compound used in the preparation of the procatalyst composition according to the invention is preferably an organic or inorganic titanium compound, which is at the oxidation degree 3 or 4.

Also other transition metal compounds, such as vanadium, zirconium, chromium, molybdenum, and tungsten compounds, can be mixed with the titanium compound, if necessary. The titanium compound usually is halide or oxyhalide, an organic metal halide, or a purely metal organic compound, in which only organic ligands have been attached to the transition metal. Particularly preferable are the titanium halides, expressly  $\text{TiCl}_4$ .

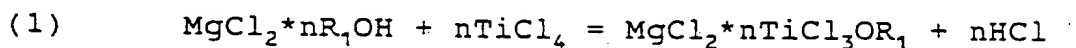
The alkoxy group of the phthalic acid ester used comprises at least 5 carbon atoms. As the above-mentioned good properties become accentuated when the alkoxy group becomes longer, it is advantageous if the alkoxy group of the phthalic acid ester comprises at least 8, and preferably 10 carbon atoms. Thus, among others propylhexyl phthalate (PrHP), in the alkoxy group of which there are 6 carbon atoms, dioctyl phthalate (DOP), in the alkoxy group of which there are 8 carbon atoms, di-isodecyl phthalate (DIDP), in the alkoxy group of which there are 10 carbon atoms, and ditridecyl phthalate (DTDP), in the alkoxy group of which there are 13 carbon atoms, can be used as the ester. The molar ratio of phthalic acid ester and magnesium halide is in the synthesis preferably of the size class about 0.2.

It is also preferable if the ester of the phthalic acid used acts as the so-called electron donor of the catalyst composition with the intention to improve the activity and the stereospecificity of the polymer.

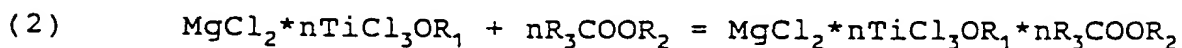
The transesterification can be carried out e.g. by selecting a phthalic acid ester - a lower alcohol pair, which spontaneously or by the aid of a catalyst, which does not damage the procatalyst composition, transesterifies under normal preparation conditions of the catalyst. Often it is, however, necessary to use an elevated temperature in order to achieve transesterification. Hereby, it is preferable to carry out the transesterification at a temperature which is between 110-150° and preferably between 130-140°C.

As the boiling point of the liquid  $\text{TiCl}_4$  is about  $136^\circ\text{C}$  under normal pressure, a treatment with it or the so-called titanification can normally be carried out only at a temperature lower than that. As usually hydrocarbon solvents, such as heptane, hexane, or pentane, the boiling point of which is remarkably higher, are used as the titanification intermediate agent, the titanification temperature is in practice below  $100^\circ\text{C}$ , where transesterification does not take place. Thus, in order to achieve transesterification, solvents having a higher boiling point should preferably be used and e.g. nonane (bp.  $151^\circ\text{C}$ ) and decane (bp.  $174^\circ\text{C}$ ) are recommendable. Hereby, it is possible to approach the boiling point of  $\text{TiCl}_4$  or even exceed it as a titanification temperature, whereby a simultaneous transesterification reaction becomes possible.

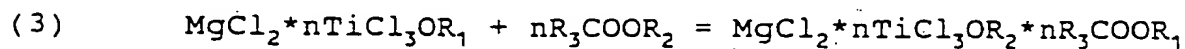
According to one embodiment the transesterification takes place so that the adduct  $\text{MgCl}_2 \cdot n\text{R}_1\text{OH}$  of magnesium dichloride and lower alcohol, in which  $n$  is 1-6, is treated with a titanium compound, e.g. titanified with  $\text{TiCl}_4$ , whereby apparently the following reaction takes place:



When the donor, i.e. the ester of the phthalic acid, is added to this titanified carrier it is very likely that an adduct of all the components is produced:



As this adduct can be transesterified at a temperature above  $110^\circ\text{C}$  and preferably at a temperature of over about  $130^\circ\text{C}$ , the ester groups  $\text{R}_1$  and  $\text{R}_2$  exchange positions.



When the waste matter of the catalyst is removed by extraction an adduct of the carrier and the ester donor is

obtained, in which the group derived from the alcohol of the ester has been exchanged:



If enough titanium remains on the carrier, it acts as an active part of the procatalyst. Otherwise, a new titanification is carried out after the above-mentioned treatment in order to ascertain a high enough titanium

content and thus activity. The titanium separation of the formula (4) mainly concerns with the inactive part of the titanium.

Thus, in the present invention a procatalyst composition intended for the polymerization of olefins has been achieved, the titanium and donor contents of which are low in regard to the activity of the catalyst. The procatalyst composition contains according to one embodiment 2.5% by weight of titanium at the most and preferably 2.0% by weight of titanium at the most. Its molar ratio donor/Mg preferably is between 0.03-0.06 and/or its donor content is between 4 to 6% by weight. According to one embodiment of the invention the alkoxy group of the phthalic acid comprises at least 8 carbon atoms and the activity of the procatalyst composition when triethyl aluminum is used as the catalyst and cyclohexylmethyl dimethoxy silane is used as the outer donor is at least about 800kg PP/g of Ti.

According to the invention the procatalyst composition intended for the polymerization of olefins is preferably prepared by

a) bringing an adduct of  $\text{MgCl}_2$  and a lower alcohol to react with  $\text{TiCl}_4$ ,

b) bringing the product of the stage a) to react with an ester of the phthalic acid under conditions where a transesterification takes place between the ester of phthalic acid and the lower alcohol,

c) washing the product.

d) bringing the end product of the stage c) to optionally react with  $\text{TiCl}_4$  (i.e. another treatment with  $\text{TiCl}_4$ ).

The invention also concerns with the use of the above-described procatalyst composition for the polymerization of propene so that the polymerization is carried out in the presence of an organometallic cocatalyst, such as tri-lower alkylaluminum, and preferably an outer donor like cyclohexylmethyl dimethoxy silane. The polymer produced contains, among others, a little titanium and donor and resembles morphologically the catalyst composition used.

In the following a method for the polymerization of olefins is presented as an example case. In this method propene is polymerized with a catalyst composition, in which a spray-crystallized  $\text{MgCl}_2 \cdot x \text{ EtOH}$  adduct is used as the carrier, which adduct has then been titanificated with  $\text{TiCl}_4$  in a hydrocarbon solvent in the presence of dialkylphthalates of different length. By the aid of the procatalyst composition thus obtained and the trialkylaluminum cocatalyst (triethylaluminum TEA) and the outer donor (cyclohexylmethyl dimethoxy silane CMMS) propene was polymerized in a hydrocarbon solvent. If a titanification temperature high enough is used a transesterification takes place between the ethoxy groups derived from the carrier adduct and the long alkyl groups of the donor and the donor compound produced will be diethyl phthalate (DEP). The aim of the following examples is only to illustrate the invention.

### Examples

#### Donors examined

In the test series 5 donors were tested. They have all been disclosed in table 1. The donors tested were propylhexyl phthalate (PrHP), dioctyl phthalate (DOP), di-isodecyl phthalate (DIDP), and ditridecyl phthalate (DTDP). In addition to this di-isobutyl phthalate (DIBP) was included in the test series.

Table 1The tested internal donors

5	Test	Length of the alkyl group	Donor	Molar mass g/mole	Density g/ml
	1	4	DIBP	278	1.00
	2	6	PrHP	292	0.95
10	3	8	DOP	390	0.96
	4	10	DIDP	446	0.96
	5	13	DTDP	530	0.91

Catalyst synthesis

15 0.1 mole of  $MgCl_2 \cdot x \cdot 3 \text{ EtOH}$  was suspended under inert conditions into 250ml of decane in a reactor. The solution was cooled to the temperature of  $-15^\circ\text{C}$  and 300ml of cold  $TiCl_4$  was added. Then a controlled heating to the temperature of  $+20^\circ\text{C}$  was carried out. At this temperature 0.02 mole of

20 the internal donor was added. In all the catalyst syntheses the molar ratio between the donor and the  $MgCl_2$  was 0.2. When all the synthesis reagents were present, the temperature was raised to  $135^\circ\text{C}$ . Both the first and the second titanification was carried out at this temperature. The catalyst synthesis was ended by carrying out a wash for the reaction mixture.

In order to find out the particle size of the procatalyst produced the particle size distribution was measured out and microscope pictures were taken of each sample. Moreover, the

30 chemical composition of the procatalysts was measured by analyzing their Ti, Mg and donor contents. Also X-ray diffraction spectra were taken for the examination of the changes taking place in the crystal structure.

Test polymerization

35 For all the catalysts a test polymerization was carried out under the following polymerization conditions. As the reaction vessel was used a 2-liter bench reactor. In the test polymerization 20 to 30g of procatalyst was used. This

amount was mixed with 620 $\mu$ l of triethylaluminum and 200 $\mu$ l of a 25% solution of CMMS in 30ml of heptane. The polymerizations were carried out at a temperature of +70°C and in a propene monomer pressure of 10 bar. The partial hydrogen pressure was 0.2 bar during the polymerization. The polymerization lasted 3 hours. In the beginning of the test a prepolymerization took place in those ten minutes when the temperature and the pressure rose to the desired polymerization conditions. The activity was measured on the basis of the polymerization yield. The soluble portion of the polymer was measured by evaporating the measured amount of the polymerization solution. By using these standard polymerization conditions a polymer material was prepared, the MFR (...) of which was about 8.

#### Characterization of the polymerizing batches

The bulk density and the particle size distribution (PSD) of all the polymerization drive were measured. The isotacticity was measured by the aid of heptane eluation and the isotacticity index was determined from the results obtained from the evaporation residue measurings. The melt index was measured at the temperature of 230°C using a weight of 2.16kg. Microscope pictures were taken from all the polymerization batches for documentation and comparison purposes. Differential scanning calorymetry curves (DSC-curves) were taken for the characterizing of the melt behaviour of the material. The specific surface and the pore volume distribution were measured by the aid of a Hg-porositymetry equipment.

#### The results

In table 2 the codes of all the catalysts and the corresponding polymers are presented.

Table 2The symbols of the catalysts and polymers used in the test

	Length of the alkali group	Symbol of the catalyst	Symbol of the polymer
5	4	C-C-4	1 PP-C-4
	6	C-C-6	2 PP-C-6
	8	C-C-8	3 PP-C-8
	10	C-C-10	4 PP-C-10
10	13	C-C-13	5 PP-C-13

The titanium content of the catalyst

The magnesium and titanium contents of the catalyst are shown in table 3. The titanium content has also been disclosed in fig. 1. The results shew that when the Mg-content remained substantially unchanged a systematic decrease of the Ti-content was observed in the catalyst series. The longer was the alkyl chain of the electron donor's alkoxy group, the smaller was the Ti-content of the final procatalyst. The Ti-content of the last catalyst of the series was 1.6% by weight. This is a 60% smaller value than the 4% value which was achieved in the standard synthesis and even 30% lower than the titanium content found in commercial high-yield catalysts. These results shew that the combination of transesterification and the washing effect of  $\text{TiCl}_3 \cdot x \text{OEt}$  worked better when higher phthalic acid esters were used.

Table 3The Mg- and Ti-content of the catalysts

	Length of the alkyl chain	Mg (%)	Ti (%)
	4	18.1	2.4
	6	20.8	2.2
	8	22.0	1.9
35	10	20.0	1.9
	13	17.3	1.6

The catalyst yield of the catalyst synthesis

The respective catalyst yields of each catalyst synthesis have been shown in table 4 and the results have been disclosed graphically in fig. 2. The same trend is noticeable as in the first measuring, i.e. that when the phthalate alkyl chain grew longer and the titanium content became smaller also the yield of the catalyst decreased. The decrease of the yield is very insignificant, only about 25% and is explained by the decrease of the  $\text{TiCl}_4$ -content of the catalyst and by the decrease of weight which occurs when the electron donor having a higher molar mass is exchanging to an electron donor having a smaller molar mass. The decrease of the catalyst yield is also explained by the decrease of the total donor content.

Table 4The catalyst yield of the catalyst synthesis

Length of the alkyl group	Yield (g)
4	13.3
6	10.0
8	12.4
10	9.1
13	9.2

The donor content of the catalysts

The donor content of the catalysts was measured liquid-chromatometrically by HPLC-method. The results are listed in table 5 and they have been presented graphically in fig. 3. In all catalysts a small fraction of mixed esters were observed and a small fraction of phthalic acid anhydride. As appears from fig. 3 the transesterification was not complete as far as the first catalyst of the series is concerned. The transesterification degree of DIBP was only 70%. This means that DIBP does not become transesterified completely at a temperature of 135°C. In all the other syntheses the transesterification was complete. In their products only marks of the original ester were found. The amount of the transesterified diethyl phthalate DEP found in the

catalysts was about constant and close to 5%. This corresponds to the D/Mg ratio 0.03 to 0.04 (D = donor), which is even a lower value than what was achieved when DIBP was transesterificated at the temperature of 143°C.

These results show that the transesterification improves if longer alkyl chains are used in phthalic acid esters. It appears simultaneously that a low electron donor/MgCl<sub>2</sub> molar ratio is achieved.

Table 5

The donor composition of the catalysts. PA = acid anhydride and IE = mixed esters produced during the transesterification

Length of the alkyl group	Original (%)	DEP (%)	PA (%)	IE (%)
4	3.6	4.0	1.3	1.0
6	0.2	5.3	0.3	0.9
8	0.3	4.8	0.7	0.4
10	0.4	5.3	1.1	0.5
13	0.2	5.9	0.7	0.4

The particle size distribution (PSD) of the catalysts

Also the PSD of the catalysts was measured and the results are shown in table 6. In fig. 4 there has been presented the average particle diameter of the portion which comprised over 90% of the particles as a function the length of the donor's alkyl chain. The results show that when the donor composition changes also the PSD changed greatly.

Simultaneously, it could be noted that the catalyst particles agglomerated when higher phthalic acid esters were used. This agglomeration can be seen in the PSD-curves of the figures 5, 6, and 7 and in the microscope pictures of figures 8, 9, and 10. The results also shew that the agglomeration decreased a little with higher phthalic acid esters. By using DIDP (C = 10) catalyst particles with a very beautiful shape were obtained, the diameter of which was about 140µm. This appears from figure 10.

Table 6

Particle size distribution of the catalysts

	Length of the alkyl group	D (0.9) $\mu\text{m}$	D (0.5) $\mu\text{m}$	D (0.1) $\mu\text{m}$
5	4	117	62	34
	6	127	68	36
	8	218	76	17
	10	138	56	18
10	13	140	69	36

The X-ray diffraction spectra of the catalysts

As a result of the transesterification a new procatalyst structure was produced, which appears from the double peak at 13 to 15°. For the following of the influence of the higher phthalate esters the X-ray diagrams were taken of all catalysts of the test series. The crystal dimensions derived from the diagrams are listed in table 7 and the results have also been presented in figure 11. According to the results the crystal became systematically broader when the alkyl chain became longer. With DTDP was achieved 25% broader crystals than what was achieved with DIBP.

The X-ray diffraction spectrum of the catalyst C-C-6 has been presented in figure 12. According to the diagram recrystallization appears in  $\text{MgCl}_2$ -crystal lattice, which becomes apparent in the sharpening of the crystal peak at points 30° and 35°. Also the formation of the double peak at point 13 to 15° can be seen.

Table 7

The crystal dimensions of the  $\text{MgCl}_2$  material of the catalysts

	<u>Section planes</u>			
	Length of the <u>alkyl group</u>	Height (nm)	Breadth (nm)	Growth %
35	4	1.8	7.9	0
	6	2.1	7.9	0
	8	1.9	8.4	6
	10	2.3	9.3	18
	13	2.2	9.8	24

The surface area and the pore volume of the catalysts

From the catalysts were measured both the surface area and the pore volume. The results have been listed in table 8. According to the results the surface area of the catalysts remained nearly unchanged independent on the donor used in the synthesis. The specific surface achieved was of the size class about 300m<sup>2</sup>/g. The pore volume, on the other hand, grew when transferring into donors with longer chains. In the last catalyst of the series an increase of as much as 60% was observed. The growth of the pore volume can partly be explained by the agglomeration of the catalyst particles.

Table 8

The specific surface area and the pore volumes of the catalysts

Length of the alkyl group	Surface area (m <sup>2</sup> /g)	Pore volume (ml/g)
4	348	0.524
6	316	0.738
8	311	0.581
10	339	0.776
13	292	0.814

Activity of the catalysts

All the catalysts were test polymerized in the above-mentioned conditions. The results have been presented in table 9 and figure 13. The activity based on the weight of the catalyst and the polymer remained constant for the whole catalyst series and was about 16kg/g cat. When expressed in unit kg PP/g Ti the activity systematically. This was due to the fact that the Ti-content decreased correspondingly when transferring into higher phthalic acid esters. Thus, the activity value 1019kg PP/g Ti was obtained for the last catalyst of the series. When decane was used as the activation medium the activity of the catalyst was a little smaller.

Table 9Activity of the catalyst

Length of the alkyl group	Activity (kg PP/g cat.)	Activity (kg PP/g Ti)
4	16.6	692
6	15.6	709
8	16.2	853
10	16.3	874
12	16.3	1019

The particle size distribution (PSD) of the polymers

In table 10 the PSD of the polymers has been presented together with the total amount of the fine cut i.e. the particles below 1mm. The amount of the fine cut has also been presented graphically in figure 17.

The PSD results of the polymers follow the same model as the PSD results of the catalysts. This appears from the PSD diagrams of figures 14, 15, and 16.

Table 10Particle size distribution of the polymers

Length of the alkyl	% < 2.0 mm	% < 1.0 mm	% < 0.5 mm	% < 0.18 mm	% < 0.10 mm	% < 0.056 mm	Rest (%)
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4	12.0	67.4	18.5	1.8	0.2	0.1	20.6
6	10.7	71.3	17.7	0.2	0.1	0.0	18.0
8	95.0	3.1	1.1	0.5	0.2	0.1	1.9
10	14.6	69.4	15.5	0.5	0.2	0.1	1.9
13	52.1	30.4	17.1	0.2	0.1	0.1	17.5

The bulk density of the polymers

The bulk density decreased when higher phthalic acid esters were used in the transesterification synthesis. The results have been listed in table 11 and presented in figure 18.

Table 11The bulk density of the polymers

---

	<u>Length of the alkyl group</u>	<u>Bulk density (g/ml)</u>
10	4	0.46
	6	0.44
	8	0.33
	10	0.37
	12	0.39

The melt index of the polymers

The chain length of the ester did not have much significance for the melt index. The results have been presented in table 12.

Table 12The melt index of the polymers

---

	<u>Length of the alkyl group</u>	<u>Melt index (2.16kg)</u>
25	4	10.5
	6	9.3
	8	10.0
	10	7.3

Molecular weight of the polymers

No systematic changes of the molecular weight distribution could be observed when the ester changed. All results have been listed in table 13. The results correspond to the results normally obtained in standard polymerization.

y pattern of the catalyst C-C-6, in which inter-  
has been transesterified to DEP. A double peak is  
13-15°.

alyst activity as a function of the alkyl group  
n the donor. Curve (A) refers to the unit kg PP/g  
(B) to the unit kg PP/g Ti.

article size distribution of the polymer PP-C-4

article size distribution of the polymer PP-C-8

article size distribution of the polymer PP-C-13 (C

total amount of fines fraction ( $d < 1 \text{ mm}$ ) as a func-  
alkyl group chain length in the donor.

Bulk density of the polymers as a function of the  
chain length in the donor.

DSC (differential scanning calorimeter) curve of the  
-C-4.

10.0 °C/min

n

34 mJ

07.5 J/g

61.6 °C

-1.2 W/g

51.4 %

209.0 J/g

1. DSC curve of the polymer PP-C-8.

10.0 °C/min

ion

352 mJ

108.3 J/g

mediane diameter of

lume Diameter of

/g) pore, (μm)

1.2

4.9

1.5

26.3

18.8

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Table 13Molecular weight distribution of polymers

	Length of alkyl group	Mn	Mw	Mv	D
5	4	58,000	173,000	223,000	4.7
	4	58,800	274,000	222,000	4.7
	6	56,000	281,000	225,000	5.2
10	6	55,200	289,000	232,000	5.2
	8	60,100	273,000	221,000	4.6
	8	60,700	279,000	228,000	4.6
15	10	73,800	331,000	269,000	4.5
	10	74,600	334,000	270,000	4.5

The DSC measuring results of the polymers

20 In table 14 the melting points, the crystallization points and the crystallinity percentages of the polymers have been listed. Neither could it be observed here any systematic dependency of the esters used. The melting point is about 161°C and the crystallizing temperature about 114°C. The crystallinity was about 51-52%. In figures 19, 20, and 21 some melting curves have  
25 been presented.

30 It can generally be said that a correlation prevails between the titanification temperature and the crystallization temperature of the catalyst. A higher titanification temperature gives purer catalyst and more homogeneous polypropene. This, on its part, increases the crystallinity of the polymer and decreases the crystallizing temperature. The correlation between the titanification temperature of the catalyst and the crystallizing temperature of the polymer is schematically presented in figure  
35 22.

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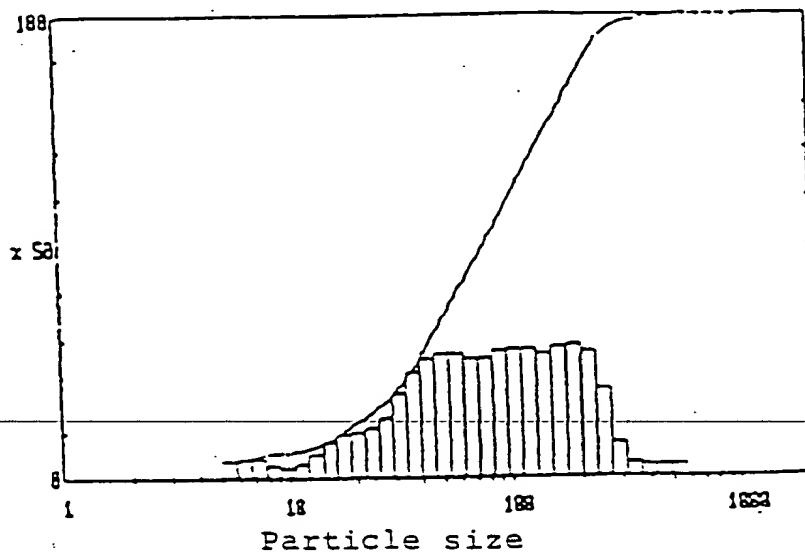


Fig. 5

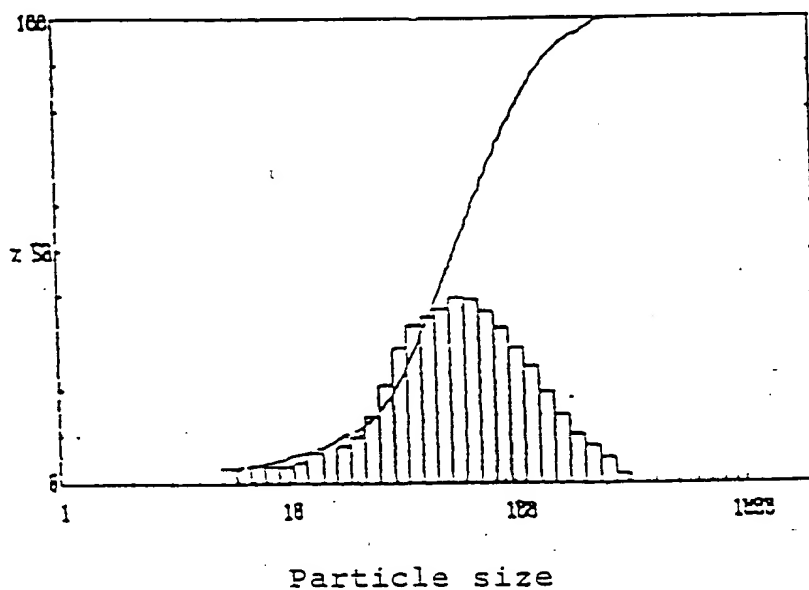


Fig. 6

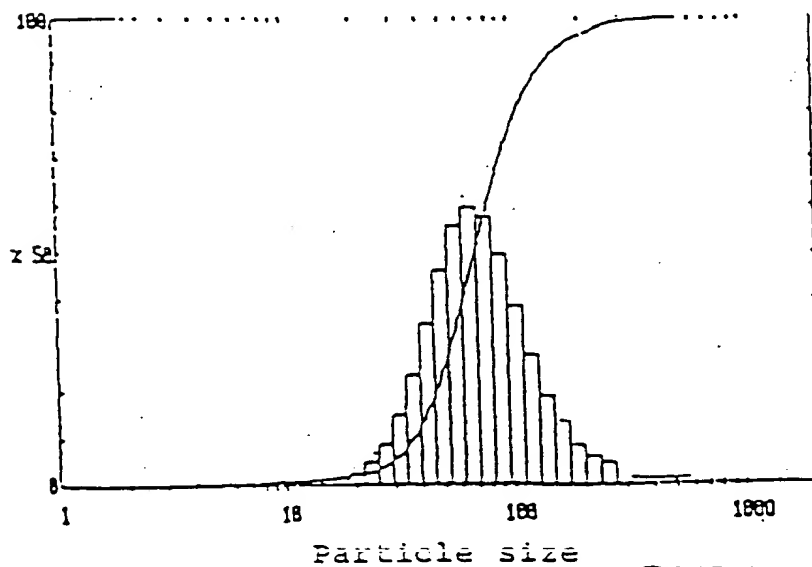


Fig. 7

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Fig. 8

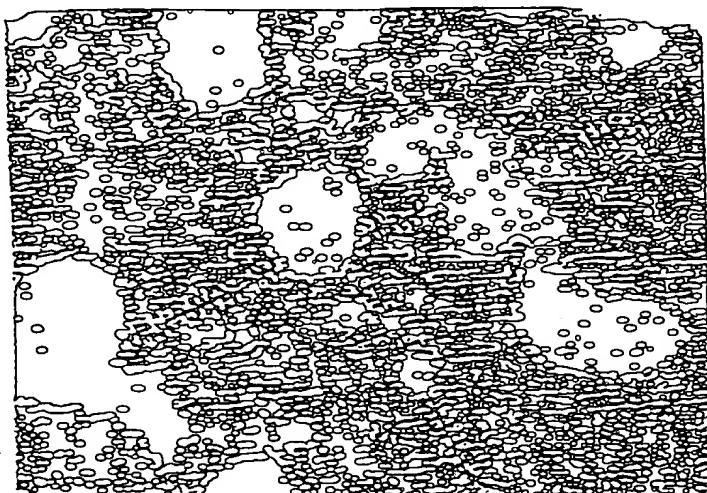


Fig. 9

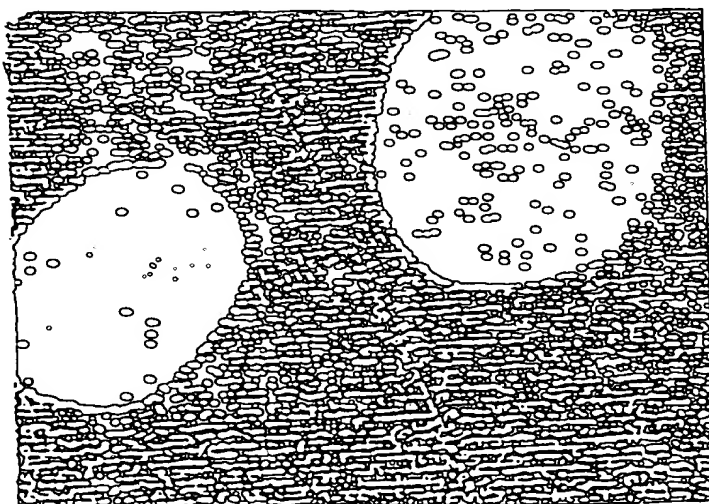


Fig. 10

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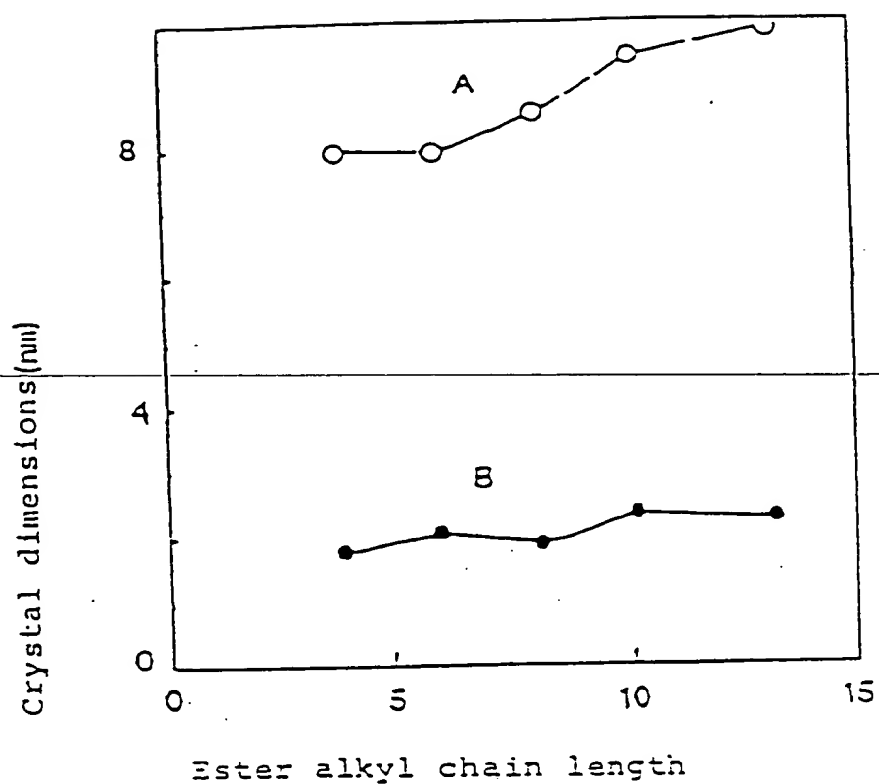


FIG. 11

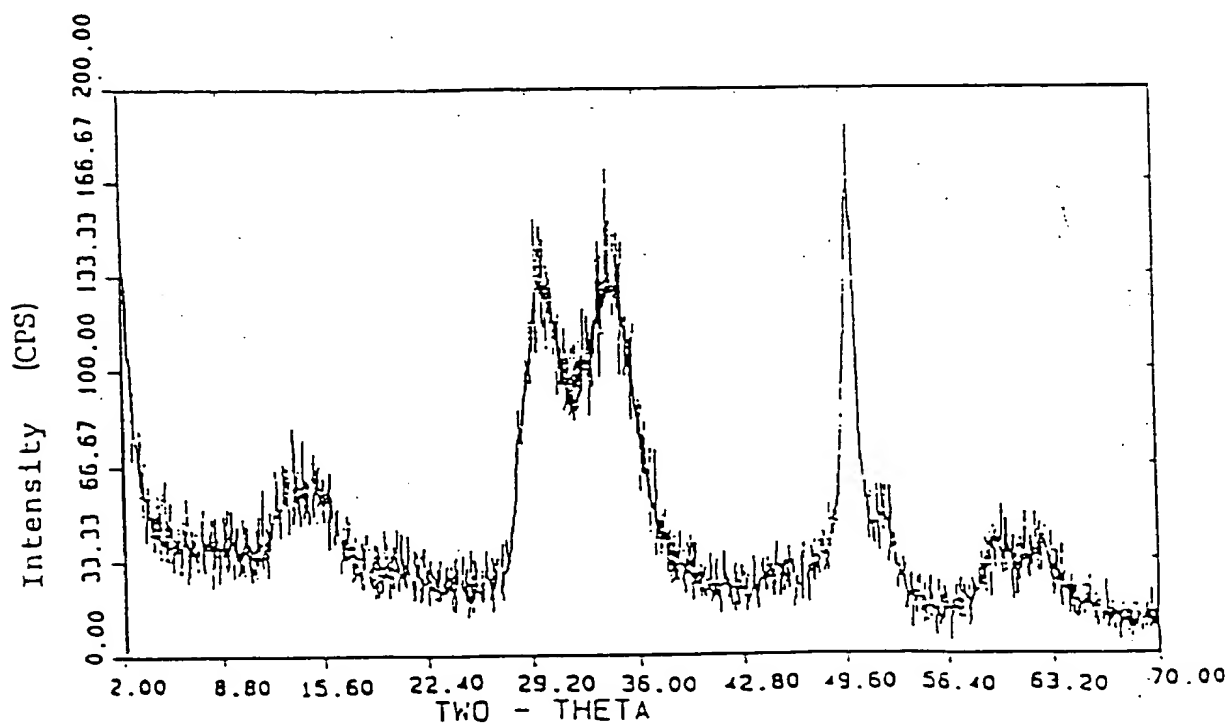


FIG. 12

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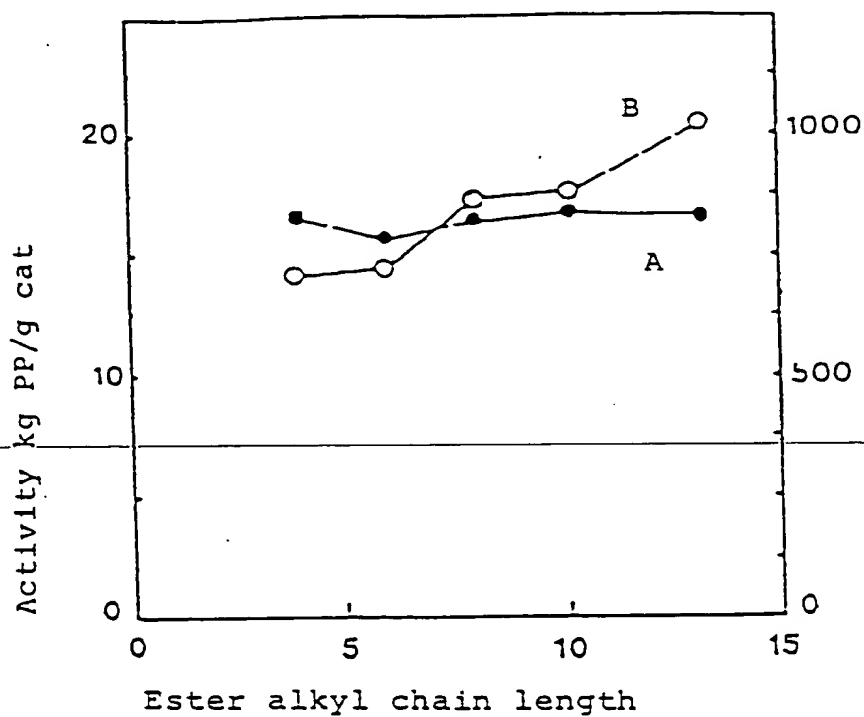


FIG. 13

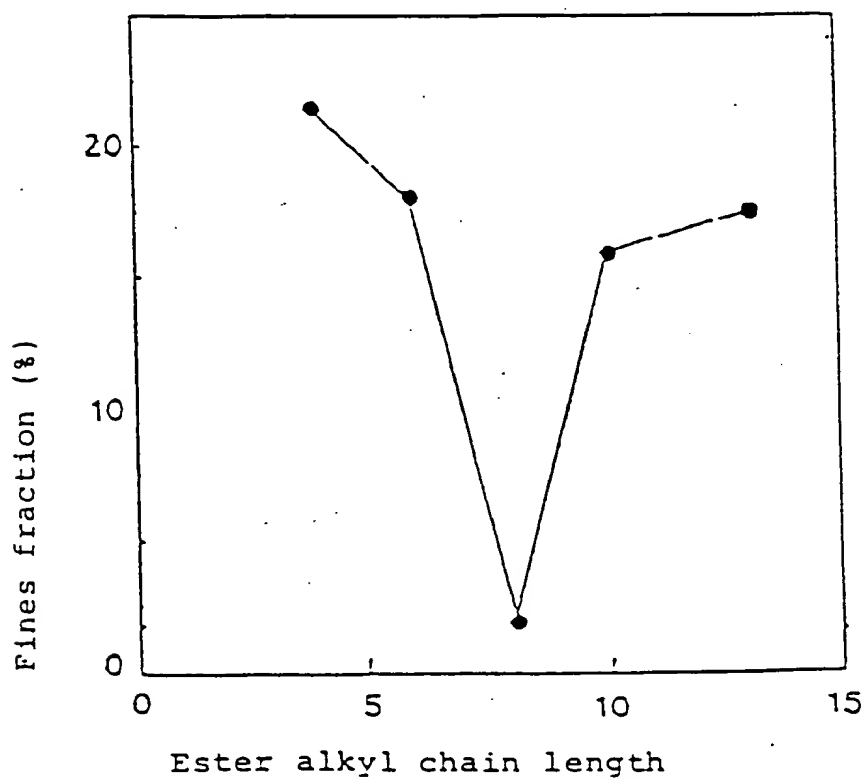


FIG. 17

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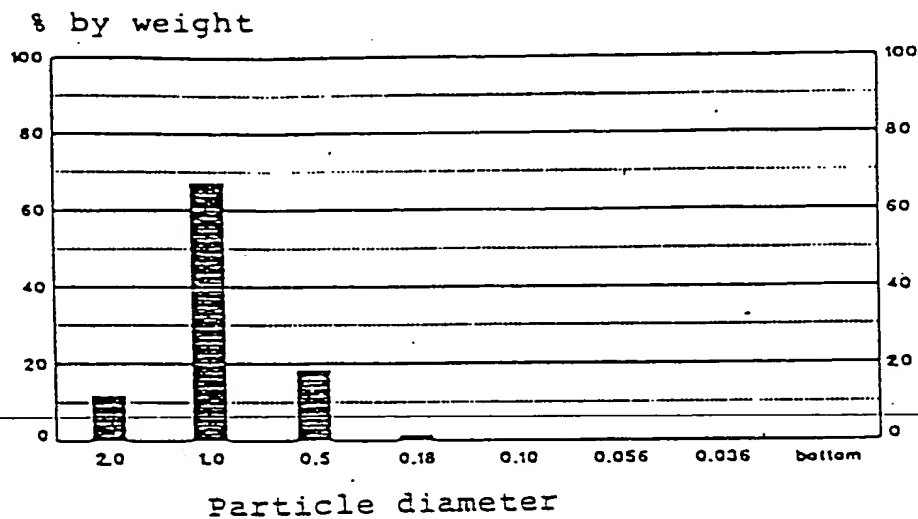


FIG. 14

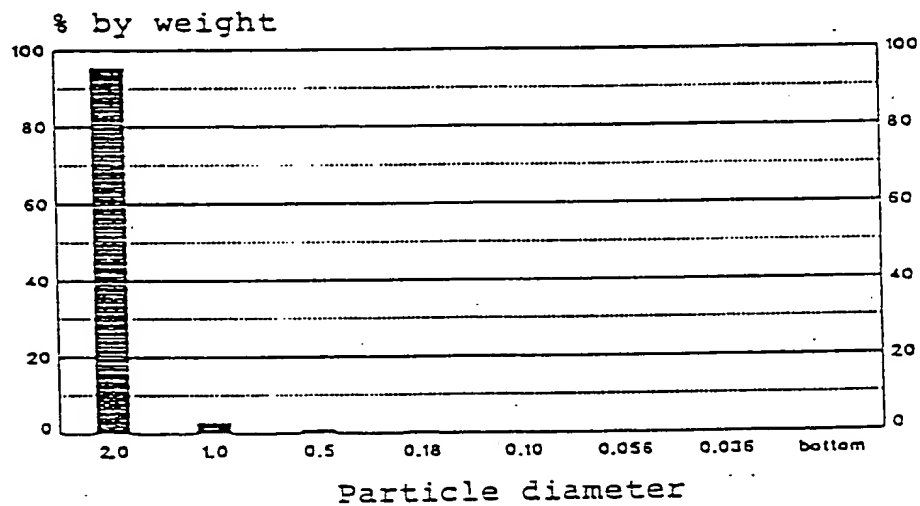


FIG. 15

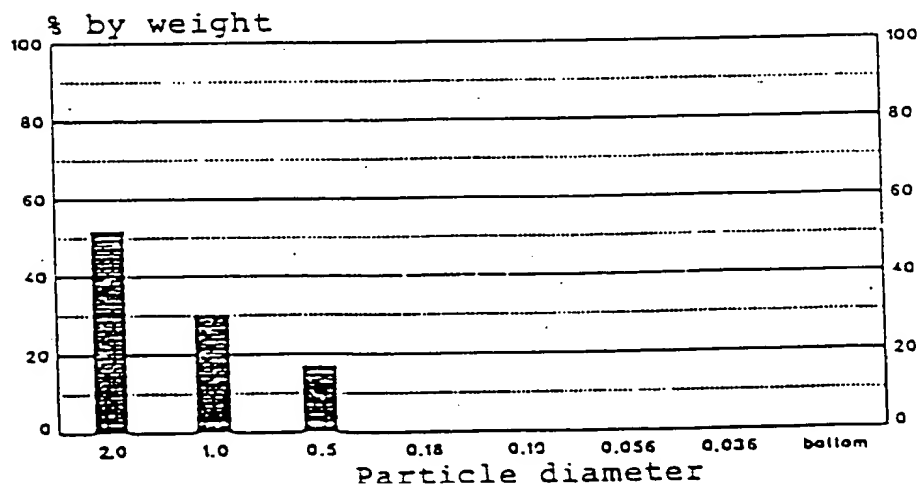


FIG. 16

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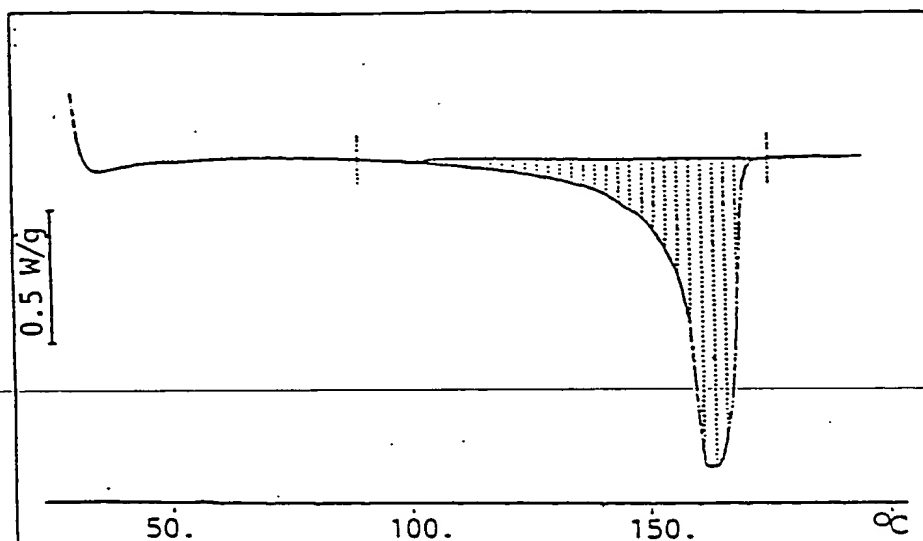


Fig. 19

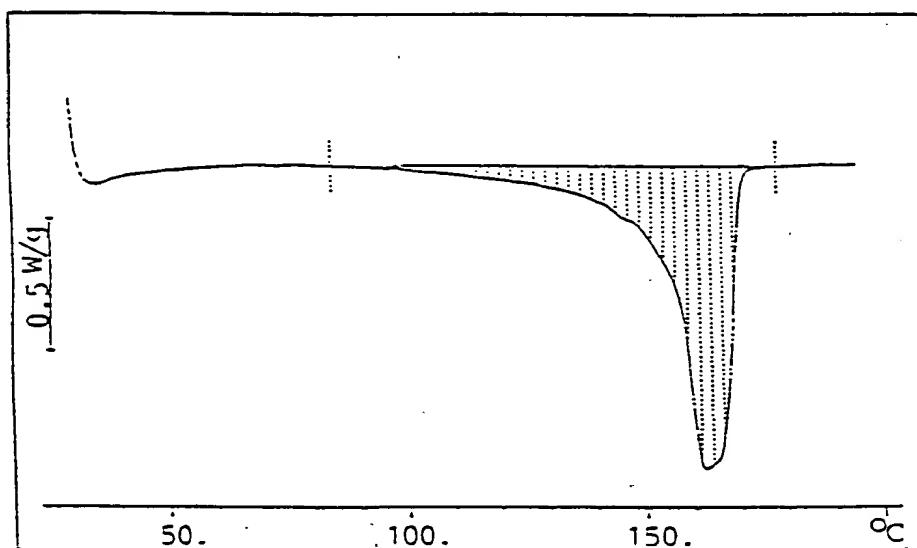


Fig. 20

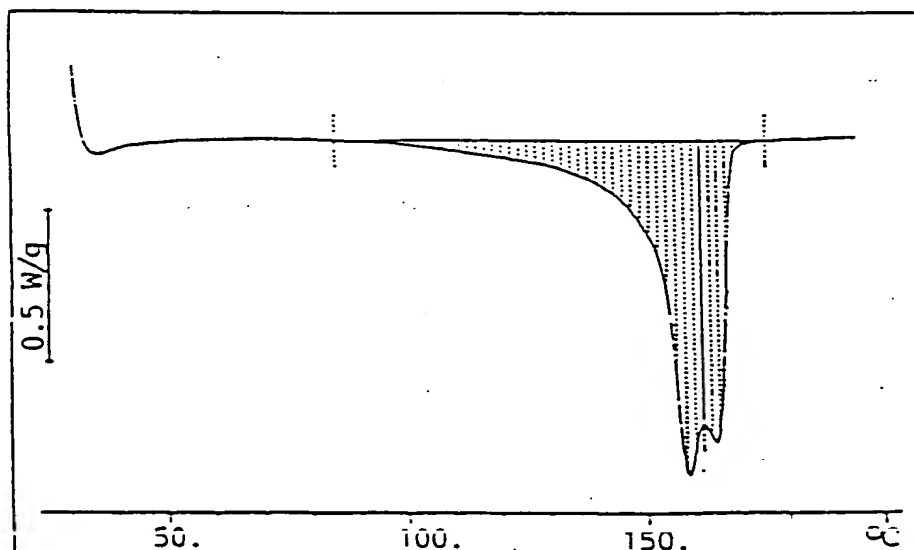


Fig. 21

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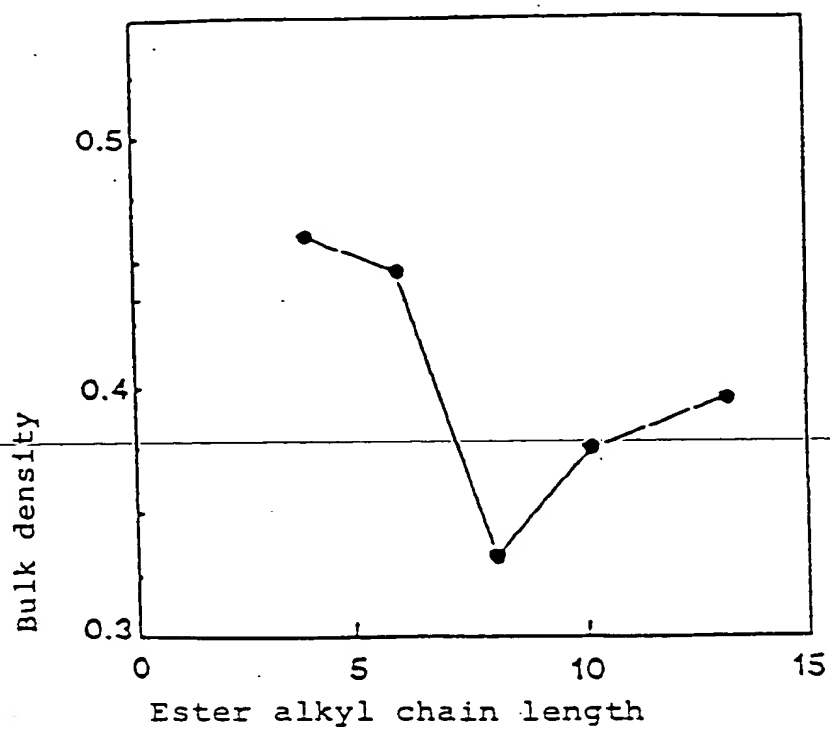


FIG. 18

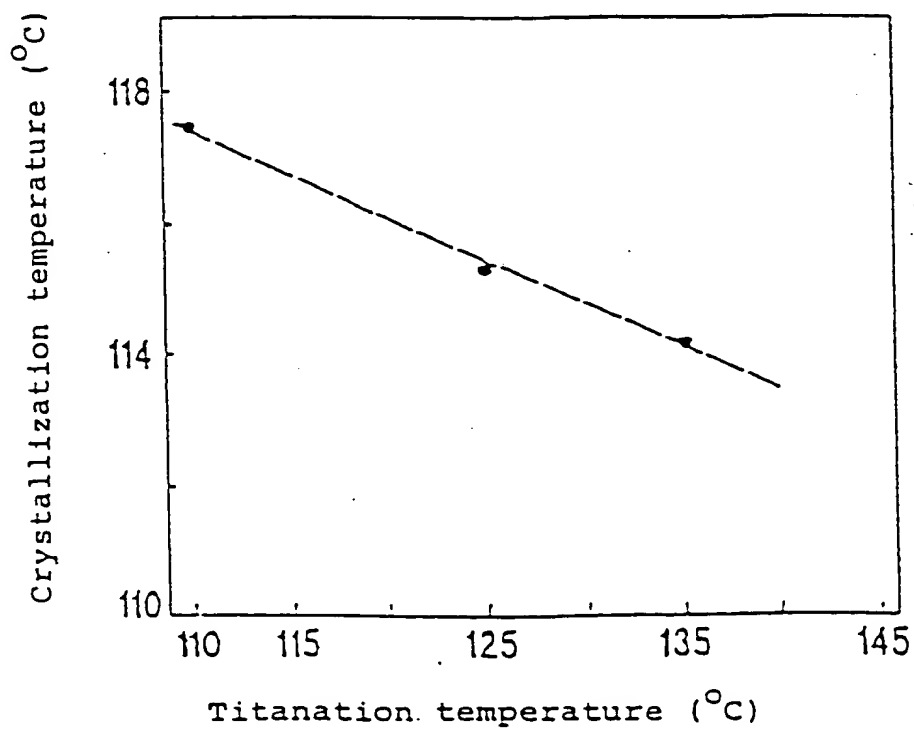


FIG. 22

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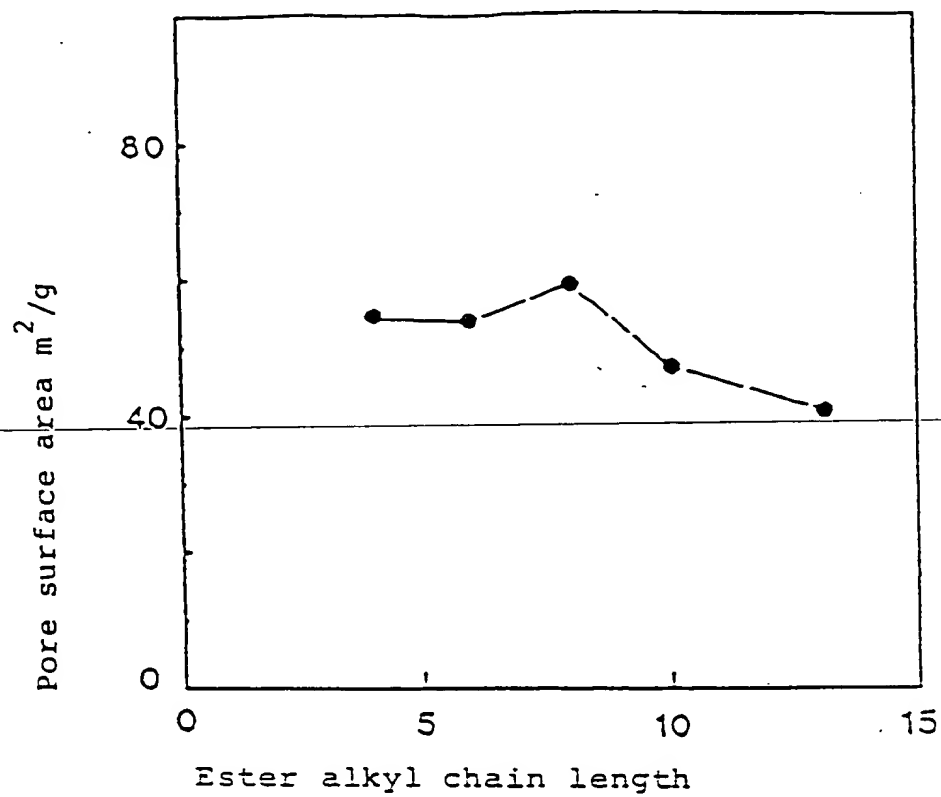


FIG. 23

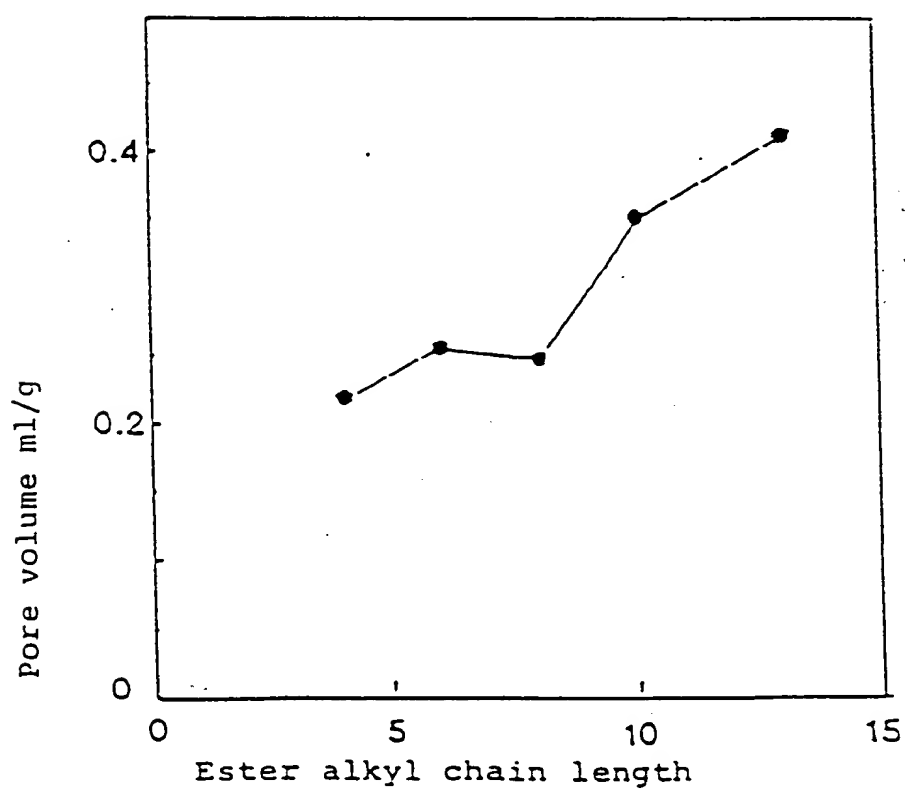


FIG. 24

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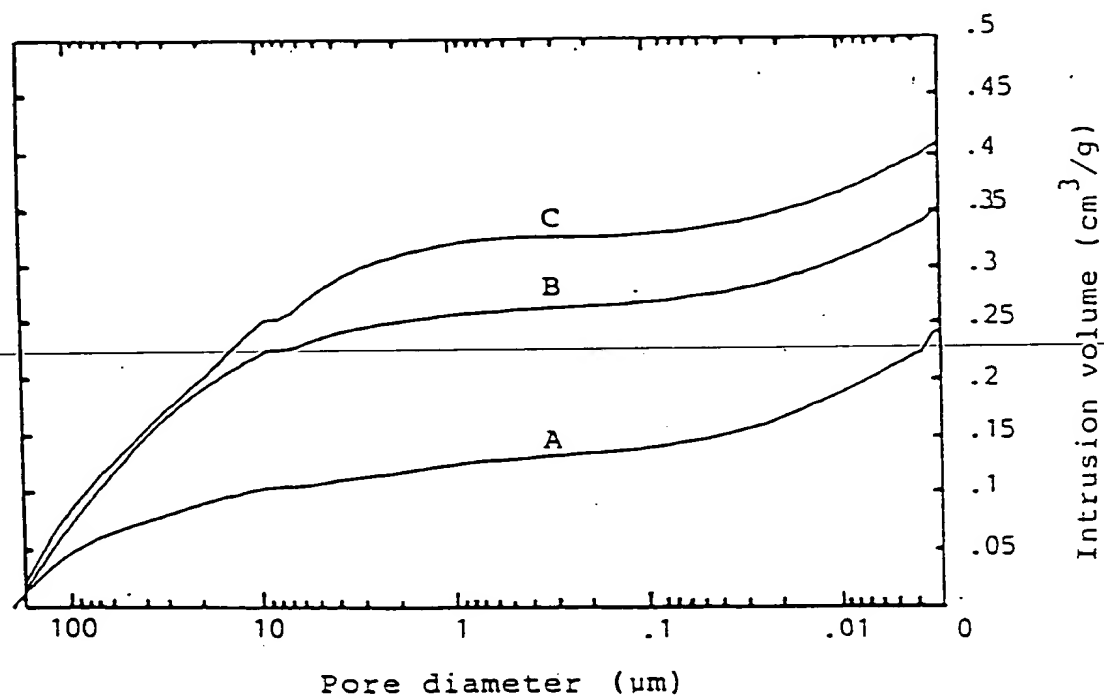


FIG. 25

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ANNEX TO THE INTERNATIONAL SEARCH REPORT  
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